

## Terpolymers. II. Mechanical Properties and Transition Temperatures of Terpolymers of Vinyl Stearate, Vinyl Acetate, and Vinyl Chloride

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### Synopsis

Vinyl stearate was studied as a major internal plasticizer in terpolymers containing vinyl acetate and vinyl chloride. The terpolymers were prepared by systematically replacing vinyl acetate by close increments of vinyl stearate starting with combinations of vinyl acetate and vinyl chloride, in increments, over all compositions. For comparison of properties, a complete range of copolymers of vinyl stearate and vinyl chloride, as well as mixtures of poly(vinyl chloride) and di-2-ethylhexyl phthalate (DOP) were also made. The external plasticizer was more efficient in reducing the glass temperature than was vinyl stearate. The decline in  $T_g$  with weight fraction of plasticizer was linear for the copolymers and terpolymers but concave downward with the liquid diluent. The linear decline was shown to involve mere additivity of the free volume contributed by each side-chain methylene (or methyl) group in both vinyl esters to reducing  $T_g$ . The mechanism of the diluent system was more complex. However, the magnitude of the reduction of tensile modulus at a given weight fraction of DOP could be equaled or exceeded by the same amount of vinyl stearate, by increasing the vinyl acetate content of the base copolymer to 40 mole-% or more. Unfortunately, the ultimate strengths and elongations of internally plasticized systems were reduced more than those of the mixtures at comparable compositions. Vinyl stearate was found to markedly retard photolytic degradation compared to both vinyl acetate and the external plasticizer in unstabilized samples having nearly the same thermal treatment. The effect was greater than could be ascribed to dilution by the long alkyl group. The production of a stearyl radical more stable than the radicals initiating dehydrochlorination is suggested as a possible mechanism.

### INTRODUCTION

The properties of poly(vinyl chloride) are more frequently modified by plasticization than are those of any other polymer. In fact, 80% of all plasticizers manufactured in the nation (about 1.5 billion pounds) are blended with this polymer.<sup>1</sup> The requirements of plasticizers,<sup>2</sup> such as relative ease of solvation of the macromolecules, compatibility over a wide range of temperatures, and efficiency in lowering the glass transition

temperature, are especially well met by solvent-type plasticizers used in poly(vinyl chloride). Of special importance with this homopolymer is the existence of a network of crystallinity, which persists even at high dilution.<sup>3</sup> This network reduces creep,<sup>4,5</sup> broadens master and isochronal stress relaxation curves<sup>6-8</sup> while raising and extending their rubbery plateaus.<sup>6-10</sup> Thus the use-temperature range is extended compared to plasticized amorphous polymers.<sup>6,11</sup> However, the equally desirable property of permanence<sup>2</sup> is essentially absent in all externally plasticized systems.

Internal plasticization of poly(vinyl chloride) confers permanence ideally but adversely affects the mechanical properties. Segments of the internal plasticizer rapidly destroy crystallinity even at low inclusions.<sup>12</sup> Such segments are usually incompatible with the stiff polymer and merely function as a flexible diluent in the polymer matrix. Consequently, the isochronal curves more closely resemble those of homopolymers<sup>13</sup> and lack the greater breadth and anomalously low slope of plasticized poly(vinyl chloride).<sup>11</sup> This points to different mechanisms operating in the two modes of plasticization, a fact that has long been recognized.<sup>2,14</sup>

Internal plasticizers derived from the higher fatty acids and alcohols, because of the lower glass transition temperatures of their homopolymers,<sup>15,16</sup> are more efficient than those derived from lower homologs. Vinyl stearate and the vinyl esters of shorter-chain fatty acids have been used to modify the mechanical properties of poly(vinyl chloride),<sup>17</sup> but only over a limited composition range. Recent work has shown<sup>18</sup> that terpolymer compositions, in which a stiff comonomer was modified by two mixed internal plasticizers, consisting of a lower and higher member of a homologous series, possessed more versatility and better physical properties than could be realized with either copolymer combination. Thus, mixtures of *n*-octadecyl and ethyl acrylates were able to efficiently plasticize acrylonitrile in terpolymers,<sup>18</sup> while the respective copolymers remained stiff over most compositions.<sup>18,19</sup> In view of the importance of plasticization in poly(vinyl chloride), a study of terpolymers involving this monomer seemed desirable.

In this investigation, copolymers of vinyl acetate and vinyl chloride, over all composition ranges, were further modified by incrementally displacing the vinyl acetate by vinyl stearate in the feed to yield terpolymers. One purpose of this study was to furnish details of changes in the glassy, transition, and rubbery regions of modulus-composition curves as plasticization was increased. Another purpose was to find the terpolymer compositions required to compensate for the greater efficiency of external plasticization, by the systematic incorporation of vinyl acetate in the base copolymers. For comparison, therefore, studies were also made of poly(vinyl chloride) plasticized by di-2-ethylhexyl phthalate (DOP) over all compositions. By using ester homologs as plasticizing comonomers in the polymeric systems, the segmental distribution of the main chain should be preserved, because the reactivity ratios of homologous series are the same.<sup>20,21</sup> The effect of the presence of vinyl stearate in these systems on

thermal and photodegradation was briefly investigated. Finally, the occurrence of an increase in moduli, conferred by increasing side-chain crystallinity at high vinyl stearate contents, was briefly followed in view of recent studies of the thermodynamics of this crystalline phase in homopolymers<sup>22</sup> and copolymers.<sup>23</sup> In a paper immediately following this one,<sup>24</sup> isochronal torsional moduli data are presented and discussed. The influence of side-chain crystallinity on increasing moduli is also treated in the next paper in greater detail.

## EXPERIMENTAL

### Monomers

The monomers were the purest available commercially. Vinyl acetate and vinyl chloride were distilled before use, the former through an efficient helix column. Vinyl stearate (White Chemical Sales, Inc.) was crystallized four times from acetone (10 ml/g) at  $-20^{\circ}\text{C}$ . The yield was 59% and the purity was 98% by gas-liquid chromatography; impurities were the near homologs.

### Polymerization Procedure

Dispersion polymerization was used exclusively. The vinyl esters, initiator (azobisisobutyronitrile, 0.05 mole-%), and poly(vinyl alcohol) solution (1%, made using degassed distilled water) were charged into pressure bottles under nitrogen. A 2-g excess of vinyl chloride was added, the excess was distilled off to further purge the bottle, and the bottles were capped. A low-solids recipe (2 ml/g total monomer) was used; monomer charge was 100 g. Polymerizations were conducted at  $50^{\circ} \pm 2^{\circ}\text{C}$  for 48 hr by tumbling in a water bath. After venting and purging the bottles, the polymers were isolated by filtration, washed free of dispersant using distilled water, and extracted at least four times with methanol (5 ml/g) at  $60^{\circ}\text{C}$  till free of monomer. Lack of turbidity of an aliquot of the methanol extract in excess water was taken to indicate completeness of extraction. The polymers were in the form of beads having diameters of 2 mm or less.

### Molecular Weights

Osmometric molecular weights were obtained by reported procedures,<sup>16</sup> except that single determinations were made for each sample. Toluene was the solvent employed; consequently, the molecular weights of polymers rich in vinyl chloride were not measured.

### Transition Temperatures

Glass transition temperatures and heats of fusion of side-chain crystallinity were obtained using a Perkin-Elmer differential scanning calorimeter by reported procedures.<sup>15,22,23</sup> Films and powders gave essentially the same results. The scans appeared to be too insensitive to detect main-chain

crystallinity, even in poly(vinyl chloride). Although only limited observations were made, a small baseline deviation which started at 150°C and appeared to be caused by dehydrochlorination may have prevented observation of this transition.

### Mechanical Properties

Mechanical properties were obtained by reported procedures.<sup>16</sup> No stabilizer or other additives were used. Consequently, milling and molding operations were done using the shortest exposure at the lowest temperature conducive to good molding. However, samples rich in vinyl chloride (around 90 mole-% or more) were somewhat colored.

### Light Stability

Sheets 1.5 in. × 6 in. of each test sample were made by milling and molding for the shortest times and lowest temperatures required for complete fusion. All unstabilized samples were milled for 3 min and molded for 3 min at 95°–125°C, the higher temperatures being necessary for the stiffer samples. Treatment of stabilized samples was the same, except that 7-min milling and 20-min molding times (10 min with pressure, 10 min with no pressure) were employed. The sheets were exposed in circulating air to a xenon arc (Fade-Odometer with xenon arc, Atlas Electric Device Co.) at black-panel 71°C for time increments up to 1200 hr or until failure. Sections were cut off from the sheets after predetermined and increasingly long exposures and examined. Failure was taken as the time required to reach a dark brown or black coloration. Color stayed relatively constant up to the time increment before failure. The color development was thereafter gradual during the failure increment.

### Calculations

All curve fitting and most other calculations were done with a computer (IBM 1130).

## RESULTS AND DISCUSSION

### General Features

The compositions and degrees of polymerization for all of the copolymers and most of the terpolymers investigated are presented in Table I. Feed compositions are listed; these were close to compositions calculated from elemental analysis by the procedures described in reference 18. Conversions were between 90% and 98%. An analysis was made of the drift in composition for the copolymers by the method of Skeist<sup>25</sup> as modified by Kruse.<sup>26</sup> Using average  $Q$  and  $e$  values for the vinyl esters taken from reference 27a, reactivity ratios for the copolymers were estimated to be  $r_1$  (VCL) = 1.36,  $r_2$  = 0.59. The computed compositions at experimental conversions were close to those from both feed and elemental analysis.

Consequently, feed compositions were used in all correlations to minimize experimental scatter.

The first 15 experiments in Table I relate to copolymers of vinyl stearate and vinyl chloride. Because they cover a wide range of copolymer compositions, they provide more detail than was previously reported for this system.<sup>17</sup> The remaining experiments concern the terpolymers, except experiments 16, 19, 22, 27, 37, and 44, dealing with copolymers of vinyl acetate and vinyl chloride. As one descends the list of copolymers, vinyl acetate progressively displaces vinyl chloride in each set. This provides the base copolymers whose vinyl acetate segments are incrementally replaced by vinyl stearate in the terpolymers. The quantity  $w_b$  in the table is the sum of the weight fractions of the vinyl esters, while  $n_b$  and  $MW_b$  are weighted side-chain lengths and plasticizing unit molecular weights, respectively, as defined in the table.

Degrees of polymerization (D.P.) were calculated from number-average molecular weights, using weighted mole fraction averages of the comonomer feed compositions. The degrees of polymerization drifted to low values at high vinyl stearate contents for all copolymers of vinyl stearate and vinyl chloride. This would be expected in view of the large monomer transfer constant for vinyl stearate.<sup>28</sup> However, high polymers were generally indicated by the data for the terpolymers.

Glass and flexural transition temperatures, heats of fusion, and mechanical properties for the same copolymer and terpolymer systems of Table I are listed in Table II. The numbers for the experiments (column 1), in both tables coincide. In addition, transition and mechanical property data for poly(vinyl chloride), externally plasticized by di-2-ethylhexyl phthalate (DOP), are given as experiments 53 through 62 at the bottom of the table. Moduli and strengths were gradually reduced to low values in the vinyl stearate-vinyl chloride copolymers (experiments 1-15), leveling off when the vinyl stearate content was in the range of 0.35 to 0.63 weight fraction. This is illustrated in Figure 1. Per cent elongations went through a maximum in this range. At higher vinyl stearate contents (0.63 to 0.95 in the table and figure), moduli rose and elongations decreased. Stiffening, caused by side-chain crystallinity, was responsible for the reversed behavior. The extent of side-chain crystallinity is reflected in the increasing heats of fusion given in the last column of Table II. The influence of crystallinity on the moduli will be dealt with more fully in the paper following this.<sup>24</sup>

Decrease in the glass transition temperature with the weight fraction of vinyl stearate,  $w_{vs}$ , for each system is shown in Figure 2. Curve 1 is for the vinyl stearate-vinyl chloride copolymers. In the other curves, the values at the ordinate apply to the vinyl acetate-vinyl chloride base copolymers, the rest, to the terpolymers. The linear portions of the solid lines are computed curves. These will be discussed more fully in the next section. The experimental data points fall close to these lines, which illustrate the downward displacement of  $T_g$  in each set as vinyl chloride is

displaced in the base copolymer. The anomalously scattered points for some of the data of curves 6 and 7 are not understood. The linear decline in  $T_g$  with increase in vinyl stearate and vinyl acetate contrasts with the data (Fig. 3) for poly(vinyl chloride) plasticized with incremental weight fractions of DOP. The greater efficiency of the external plasticizer in reducing  $T_g$  is obvious. The line is a computed curve, which will also be discussed below. The upward rise in the  $T_g$ -composition curves in Figure

TABLE I  
Compositions, Degrees of Polymerization, and Fractional Chain Lengths and Unit Molecular Weights of the Copolymers and Terpolymers

Experiment no. <sup>a</sup>	Terpolymer composition <sup>b</sup>				$w_b^c$	$n_b^d$	MW <sub>b</sub> <sup>e</sup>	$\overline{DP}_n$
	$m_{VS}$	$m_{VA}$	$m_{VCL}$	$w_{VS}$				
1	0	0	1.00	0	0			
2	0.025	0	0.975	0.113	0.113			
3	0.050	0	0.950	0.207	0.207			822.4
4	0.075	0	0.925	0.287	0.287			741.0
5	0.100	0	0.900	0.356	0.356			660.9
6	0.125	0	0.875	0.415	0.415			597.9
7	0.150	0	0.850	0.467	0.467			592.7
8	0.175	0	0.825	0.513	0.513			543.9
9	0.200	0	0.800	0.554	0.554			529.9
10	0.250	0	0.750	0.624	0.624			487.5
11	0.287	0	0.713	0.641	0.641			432.4
12	0.400	0	0.600	0.768	0.768			358.7
13	0.510	0	0.490	0.833	0.833			260.9
14	0.600	0	0.400	0.882	0.882			261.7
15	0.750	0	0.250	0.937	0.937			212.5
16	0	0.150	0.850	0	0.196	1.0	86.09	711.7
17	0.050	0.100	0.850	0.201	0.312	6.3	160.8	781.1
18	0.100	0.050	0.850	0.351	0.400	11.7	235.7	626.1
19	0	0.200	0.800	0	0.256			
20	0.050	0.150	0.800	0.198	0.363	5.0	142.2	741.9
21	0.100	0.100	0.800	0.346	0.442	9.0	198.3	606.7
22	0	0.250	0.750	0	0.315			349.4
23	0.050	0.200	0.750	0.195	0.411	4.2	131.0	725.9
24	0.075	0.175	0.750	0.273	0.450	5.8	153.4	594.9
25	0.100	0.150	0.750	0.342	0.484	7.40	175.9	590.1
26	0.150	0.100	0.750	0.456	0.541			517.3
27	0	0.400	0.600	0	0.479			597.8
28	0.025	0.375	0.600	0.100	0.516	2.0	100.2	757.0
29	0.050	0.350	0.600	0.187	0.549	3.0	114.1	737.2
30	0.060	0.340	0.600	0.218	0.561	3.4	119.8	741.2
31	0.070	0.330	0.600	0.248	0.572	3.8	125.4	691.4
32	0.075	0.325	0.600	0.262	0.578	3.9	126.6	700.0
33	0.080	0.320	0.600	0.276	0.583	4.2	131.0	663.0
34	0.090	0.310	0.600	0.303	0.593	4.6	136.6	646.9
35	0.100	0.300	0.600	0.329	0.603	5.0	142.2	635.7
36	0.125	0.275	0.600	0.388	0.625	6.0	156.2	573.1
37	0	0.600	0.400	0	0.674			977.1
38	0.010	0.590	0.400	0.039	0.683			1003

TABLE I (continued)

Experiment no. <sup>a</sup>	Terpolymer composition <sup>b</sup>				$w_b^c$	$n_b^d$	$MW_b^e$	$\overline{D.P.}_n$
	$m_{VS}$	$m_{VA}$	$m_{VCL}$	$w_{VS}$				
39	0.020	0.580	0.400	0.077	0.692			994.6
40	0.030	0.570	0.400	0.112	0.700	1.8	97.3	954.6
41	0.040	0.560	0.400	0.145	0.708	2.1	101.1	985.6
42	0.050	0.550	0.400	0.177	0.716	2.3	104.8	924.1
43	0.100	0.500	0.400	0.313	0.748	3.7	123.5	781.1
44	0	0.800	0.200	0	0.846			1408
45	0.005	0.795	0.200	0.019	0.849			1264
46	0.010	0.790	0.200	0.037	0.850			1411
47	0.015	0.785	0.200	0.055	0.853	1.3	90.3	1264
48	0.020	0.780	0.200	0.072	0.854	1.4	91.7	1229
49	0.025	0.775	0.200	0.089	0.856	1.5	93.1	1455
50	0.030	0.770	0.200	0.1057	0.858	1.6	94.5	1485
51	0.040	0.760	0.200	0.138	0.862	1.8	97.3	1401
52	0.050	0.750	0.200	0.168	0.865	2.0	100.1	1399

<sup>a</sup> Other terpolymers prepared but their data omitted from Tables I and II for economy of space were: mole fraction vinyl chloride (underlined) and vinyl stearate, respectively, in the feed; 0.800, 0.150; 0.750, 0.200, 0.225; 0.600, 0.150, 0.175, 0.200, 0.250, 0.300; 0.400, 0.150, 0.200, 0.250, 0.300; 0.200, 0.100, 0.125, 0.150, 0.200, 0.250. These data were included with the tabled data in obtaining some of the curve-fitting parameters of Table III.

<sup>b</sup> Feed compositions. Terpolymer compositions, calculated from elemental analyses by the procedure of ref. 18, agreed within experimental error. Designations are: mole fraction,  $m_i$ ; weight fraction,  $w_i$ ; subscripts: VS, vinyl stearate; VA, vinyl acetate; VCL, vinyl chloride.

<sup>c</sup>  $w_b = w_{VS} + w_{VA}$ .

<sup>d</sup>  $n_b = (m_{VS}/m_{VS} + m_{VA}) 17.0 + (m_{VA}/m_{VS} + m_{VA}) 1.0$ , where  $n$  is the number of methylene groups in the side chain of the esters.

<sup>e</sup>  $MW_b = (m_{VS}/m_{VS} + m_{VA})MW_{VS} + (m_{VA}/m_{VS} + m_{VA})MW_{VA}$ , where  $MW_i$  is the molecular weight of the monomer.

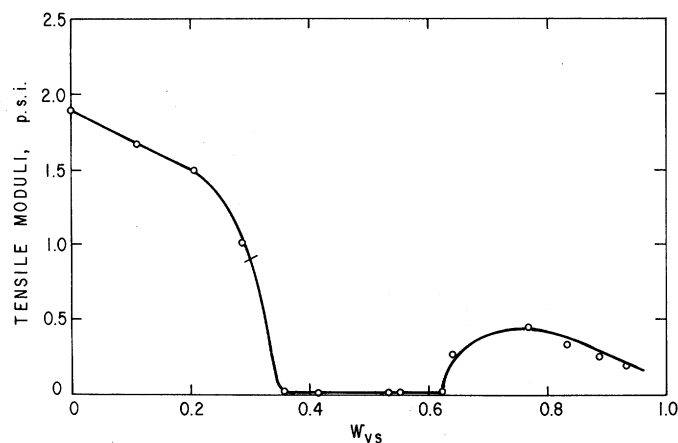


Fig. 1. Tensile moduli vs. weight fraction of vinyl stearate,  $w_{VS}$ , for copolymers of vinyl stearate and vinyl chloride, across the range of composition. Slash mark represents composition at which  $T_g$  corresponds to room temperature.

TABLE II. Transitions, Heats of Fusion, and Mechanical Properties of the Copolymers and Terpolymers

Experiment no. <sup>a</sup>	<i>w</i> <sub>vs</sub>	Transitions, °C		Flexural properties		Tensile properties			$\Delta H_f$ , cal/g
		<i>T</i> <sub>g</sub>	<i>T</i> <sub>f</sub>	Strength, psi	Modulus, psi × 10 <sup>-5</sup>	Strength, psi	Modulus, <sup>b</sup> psi × 10 <sup>-5</sup>	% Elongation	
Copolymers of Vinyl Stearate and Vinyl Chloride									
1	0	80.9	79.0	5212	2.26	6271	1.90	4.1	
2	0.113	58.9	51.0	4300	1.93	6426	1.68	6.8	
3	0.207	40.9	39.0	2446	1.14	5825	1.50	11.4	
4	0.287	24.9	21.0	1316	0.593	3122	1.02	34.6	
5	0.356	12.9	-2.0	172	0.072	2278	0.020	116.5	
6	0.415	0.9	-19.0	27	0.011	1692	0.012	168.0	
7	0.467	1.9	-34.0	21	0.008	1179	0.008	155.0	0.48
8	0.513	7.9	-24.0	32	0.013	1037	0.008	185.8	1.22
9	0.554	16.9	-31.0	65	0.027	981	0.009	206.8	1.73
10	0.624	18.9	-33.0	277	0.128	976	0.010	66.5	5.17
11	0.641	18.9	-28.0	401	0.192	1734	0.268	5.1	6.60
12	0.768	6.9	-43.0	604	0.289	559	0.450	1.8	10.43
13	0.833	6.9	-65.0	516	0.219	470	0.325	1.8	12.13
14	0.882	-22.1	—	627	0.315	306	0.256	1.4	13.11
15	0.937	-0.1	—	787	0.398	78	0.191	0.7	15.95
Terpolymers: Vinyl Chloride, Mole Fraction 0.85									
16	0	62.9	50.0	4696	2.03	9140	2.12	12.3	
17	0.201	26.9	37.0	2525	1.14	5340	1.83	6.9	
18	0.351	13.9	-10.0	135	0.050	2200	0.018	174.1	
Terpolymers: Vinyl Chloride, Mole Fraction 0.80									
19	0	66.9	42.0	4470	1.99	6074	1.88	10.7	
20	0.198	33.9	36.0	3318	1.48	6440	1.57	11.4	
21	0.346	8.9	-14.0	106	0.047	2155	0.013	214.3	

0.48  
1.22  
1.73  
5.17  
6.60  
10.43  
12.13  
13.11  
15.95



Terpolymers: Vinyl Chloride, Mole Fraction 0.75									
22	0	62.9	61.0	4775	2.14	9360	2.48	9.8	
23	0.195	26.9	37.0	3112	1.25	6920	1.88	10.2	
24	0.273	17.9	8.0	528	0.232	2154	0.106	88.9	
25	0.342	7.9	-11.0	60	0.025	1930	0.013	294.0	
26	0.456	1.9	-25.0	20	0.009	1130	0.007	287.3	0.425
Terpolymers: Vinyl Chloride, Mole Fraction 0.60									
27	0	54.9	52.0	4839	2.25	6025	2.28	4.02	
28	0.100	38.9	35.0	2768	1.11	6234	1.56	11.6	
29	0.187	25.9	23.0	1725	0.788	4560	0.908	12.4	
30	0.218	20.9	19.0	914	0.389	2010	0.711	84.8	
31	0.248	15.9	10.0	302	0.137	1807	0.017	206.6	
32	0.262	13.9	2.0	108	0.048	1556	0.014	244.8	
33	0.276	10.9	1.0	86	0.037	1745	0.012	290.8	
34	0.303	7.9	-5.0	54	0.014	1776	0.009	450.2	
35	0.329	2.9	-13.0	22	0.010	1709	0.006	252.5	
36	0.388	-5.1	-20.0	20	0.009	1310	0.004	347.4	
Terpolymers: Vinyl Chloride, Mole Fraction 0.40									
37	0	20.9	31.0	3209	1.38	5203	1.92	9.9	
38	0.039	16.9	24.0	738	0.309	3707	0.948	79.0	
39	0.077	22.9	31.0	1771	0.736	4858	1.27	14.1	
40	0.112	27.9	29.0	1742	0.720	4658	1.22	13.9	
41	0.145	22.9	21.0	909	0.384	3048	0.631	82.7	
42	0.177	16.9	5.0	62	0.028	1445	0.011	242.0	
43	0.313	-2.10	-17.0	0	0	993.0	0.002	377.0	0.430

TABLE II (continued)

Experiment no. <sup>a</sup>	<i>w</i> <sub>vs</sub>	Transitions, °C		Flexural properties		Tensile properties			$\Delta H_f$ , cal/g
		<i>T<sub>g</sub></i>	<i>T<sub>f</sub></i>	Strength, psi	Modulus, psi $\times 10^{-5}$	Strength, psi	Modulus, <sup>b</sup> psi $\times 10^{-5}$	% Elongation	
Terpolymers: Vinyl Chloride, Mole Fraction 0.20									
44	0	23.9	24.0	350.0	0.137	1857	0.517	14.0	
45	0.019	14.9	22.0	262.0	0.117	1559	0.384	67.2	
46	0.037	24.9	36.0	3305	1.38	6415	1.65	10.8	
47	0.055	24.9	29.0	1705	0.760	4219	0.991	14.0	
48	0.072	24.9	26.0	1322	0.566	2059	1.07	43.6	
49	0.089	22.9	21.0	286.0	0.109	1775	0.019	117.9	
50	0.106	20.9	23.0	648.0	0.280	2076	0.022	79.9	
51	0.138	15.9	19.0	143.0	0.053	1709	0.015	136.3	
52	0.168	11.9	7.0	41.0	0.014	1515	0.009	289.7	
Poly(vinyl Chloride) Plasticized by Di-2-ethylhexyl Phthalate (DOP)									
53	0.048°	58.9	62.0	5640	2.50	8979	2.63	5.6	
54	0.113°	41.9	49.0	4580	2.05	6385	2.29	3.5	
55	0.207°	11.9	12.0	924	0.380	4674	0.042	193.5	
56	0.287°	-2.1	-14.0	74	0.030	4120	0.031	109.7	
57	0.356°	-21.0	-30.0	20	0.008	2526	0.014	130.0	
58	0.415°	-41.1	-40.0	14	0.006	1820	0.007	233.5	
59	0.467°	-45.1	-48.0	10	0.005	1326	0.005	219.0	
60	0.554°	-53.1	-58.0		0.003	850	0.004	194.7	
61	0.624°	-63.1	-64.0		0.003	572	0.002	277.0	
62	1.000°	-87.0							

<sup>a</sup> These correspond to the same experiments listed in Table I.<sup>b</sup> Secant moduli, except when elongations exceeded 100%, where they are 100% moduli.<sup>c</sup> Weight fraction of di-2-ethylhexyl phthalate.

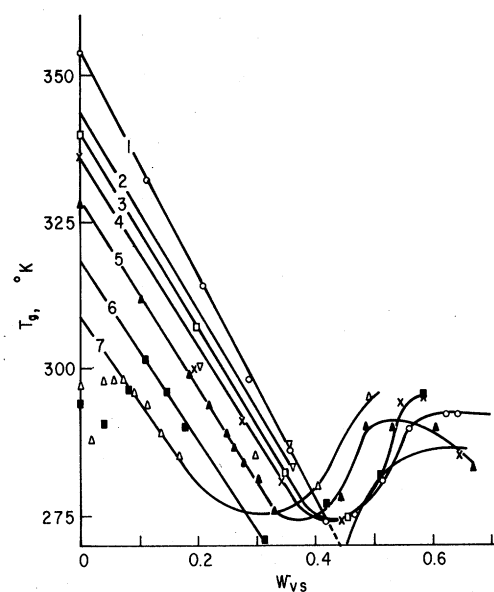


Fig. 2. Glass transition temperature  $T_g$  vs. weight fraction of vinyl stearate,  $w_{vs}$ . Designations, given as mole fraction of vinyl chloride in feed, are: (1) 1.0-0.25 (experiments 1 through 15, Tables I and II); (2) 0.85; (3) 0.80; (4) 0.75; (5) 0.60; (6) 0.40; (7) 0.20.

2 at  $w_{vs}$  greater than about 0.4 represents the usual influence of side-chain crystallinity on  $T_g$  at high crystallite levels.<sup>15</sup> Thus, the general pattern of the data specifies regular decreases in both mechanical properties and glass transitions with increase in the vinyl ester content, with the three regions of viscoelasticity (Fig. 1) clearly delineated. The relationships of both glass transition and mechanical properties to composition will be discussed in somewhat greater detail in the sections below.

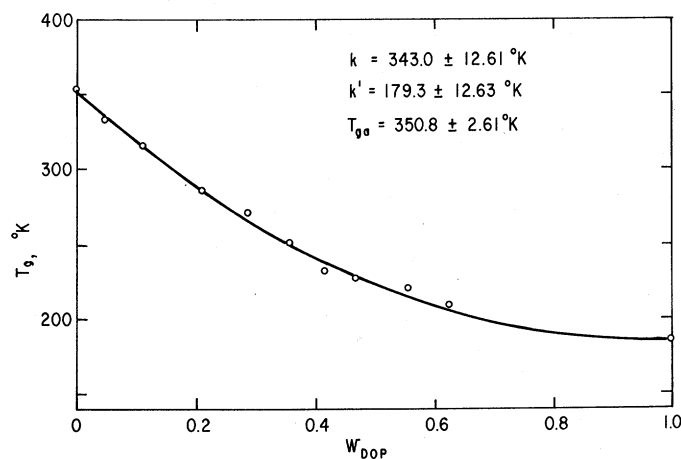


Fig. 3. Plot of glass transition temperature  $T_g$  vs. weight fraction of di-2-ethylhexyl phthalate,  $w_{dop}$ .

### Relationship of Glass Temperature to Terpolymer Composition

A general empirical equation for the change in glass transition temperature for a two component system with weight fraction,  $w_i$ , of plasticizer, whether external or internal,<sup>29,30</sup> is

$$T_g = w_a T_{ga} + w_b T_{gb} + K w_a w_b \quad (1)$$

where the subscripts  $a$  and  $b$  designate the  $T_g$  for the respective homopolymers and  $K$  is an empirical constant. In special cases, where  $K = 0$ , eq. (1) becomes

$$T_g = w_a T_{ga} + w_b T_{gb}. \quad (2)$$

This linear equation can be expressed as

$$T_g = T_{ga} - k w_b \quad (3)$$

under conditions such that  $T_{ga} > T_{gb}$ , so that  $k$  is equal to  $T_{ga} - T_{gb}$ . Equation (1) applies to many externally plasticized systems,<sup>29</sup> while eq. (3) often applies to copolymers containing internal plasticizers having long linear side chains.<sup>15,31</sup> For terpolymers, such as the present systems, where both vinyl acetate and vinyl stearate act to reduce the glass transition, the reduction in  $T_g$  with respect to the weight fraction of vinyl stearate alone can be expressed as

$$T_g = (w_{VA} T_{gVA} + w_a T_{ga}) - k w_{VS}. \quad (4)$$

In this paper,  $w_i$  is designated weight fraction and  $m_i$  is designated mole fraction. The subscript  $a$  will indicate vinyl chloride, the subscript  $b$ , the sum of the specified weight or mole fractions of vinyl esters, while the subscripts VA, VS, and DOP designate vinyl acetate, stearate, and di-2-ethylhexyl phthalate, respectively. Equation (4) accounts for the decline in  $T_g$  of the base copolymer as a decreasing intercept as vinyl chloride is successively replaced by vinyl acetate. If the decline in  $T_g$  for the terpolymers is an additive function of both vinyl stearate and vinyl acetate, the proportionality constant for the rate of change of  $T_g$  with the weight fraction of vinyl stearate,  $k$ , may be computed using

$$-k = -(dT_g/dw_{VS}) = [(T_{ga} - k' w'_{VS}) - (w_a T_{ga} + w_{VA} T_{gVA})]/w'_{VS} \quad (5)$$

where  $w'_{VS} = MW_{VS} (1.0 - m_{VCL}) / (MW_{VS} (1.0 - m_{VCL}) + MW_{VCL} m_{VCL})$  for  $m_{VCL}$  of each base vinyl acetate-vinyl chloride copolymer. This quantity is the limiting  $w_{VS}$  of eq. (4), at which the complete displacement of vinyl acetate is accomplished. The linear portion of the solid lines in Figure 2 were computed from eq. (4) after insertion of the eq. (5)-value for  $k$ ;  $T_{gVS}$  was taken as  $-111^\circ\text{C}$ ,<sup>15</sup>  $T_{gVA}$  as  $28.0^\circ\text{C}$ ,<sup>27b</sup> and  $T_{ga}$  as  $80.9^\circ\text{C}$  (Table II). The parameters, including  $k'$ , are given in Table III. These were checked by curve fitting the linear data as first-degree polynomials using the computer. The constants so obtained were close enough, within experimental error, to substantiate the assumed additivity expressed by the equations. The linear portion of the curves generally lies close to the

TABLE III  
Constants of the Various Equations

Parameter, <sup>a</sup> psi $\times 10^{-6}$	Mole fraction of vinyl chloride in monomer feed							
	1.00	0.85	0.80	0.75	0.60	0.40	0.20	Ave.
$-\gamma$								3.68
$E_m$								2.12
$-\delta$								0.0399
$TS_0$								0.0647
$-\gamma'$	9.83	12.04	10.46	12.95	14.46	13.05	21.12	13.42
$E_m'$	3.63	4.24	3.63	4.16	3.69	2.45	2.39	
$-\delta'$	0.2407	0.2091	0.2889	0.3462	0.3080	0.3544	0.9319	0.2912 <sup>e</sup>
$TS_0'$	0.1056	0.0954	0.1216	0.1302	0.0949	0.0825	0.0951	
$E_m'$ calc <sup>b</sup>	4.71	4.63	4.42	4.28	3.48	2.50	1.69	
$TS_0'$ calc <sup>b</sup>	0.1208	0.1184	0.1222	0.1164	0.0914	0.0732	0.0371	
$-\gamma''$								0.0201
$E_m''$								0.0166
$-\delta''$								0.0212
$TS_0''$								0.0215
$k$	192.2 <sup>d</sup>	170.4	168.1	165.5	159.4	151.9	144.7	
$T_{ga}$	353.8 <sup>d</sup>	343.6	340.4	337.3	328.6	318.3	309.1	
$k_{VA}$ <sup>e</sup>	56.59							
$T_{gaVA}$ <sup>e</sup>	352.4							

<sup>a</sup> Last four items in the column not multiplied by  $1 \times 10^6$ ; units of  $k$  and  $T_{ga}$  are  $^{\circ}\text{K}$ .

<sup>b</sup> Calculated using eq. (15).

<sup>c</sup> Curve-fitted constants for the relation between  $T_g$  and the weight fraction of vinyl acetate for the vinyl acetate-vinyl chloride copolymers.

<sup>d</sup> Curve-fitted constants; this is  $k'$  of eq. (5). Balance computed using eq. (4), with  $T_{ga} = w_a T_{ga} + w_{VA} T_{gVA}$ .

<sup>e</sup> Number in column 8 not included.

data points corresponding to  $w_{VS}$  lower than 0.35 to 0.40. The rise in apparent  $T_g$  beyond this region is associated with the development of side-chain crystallinity.<sup>15,22,23</sup> The curved portions of the lines in the figures were drawn through the data points; these cannot be computed by eq. (4).

The linear nature of the correlation for amorphous terpolymers contrasts (Fig. 3) with the relation found using liquid diluent. Curve fitting with the computer showed the latter data to obey the relation

$$T_g = T_{ga} - kw_{DOP} + k'(w_{DOP})^2. \quad (6)$$

Values of the constants are given in the figure. Consequently, these data follow eq. (1). The parameter  $K$  in this equation, expressing the efficiency of plasticization, may be obtained from

$$K = -k + (T_{ga} - T_{gDOP}) \quad (7)$$

using  $k$  of Figure 3,  $T_{ga} = 354.0$  (Table II) and  $T_{gDOP}$  (experiment 62, Table II) obtained directly for the pure plasticizer by DSC. The value of  $K$  was  $-175.1^\circ\text{K}$ . Consequently, the efficiency of DOP in reducing the glass transition temperature of poly(vinyl chloride) greatly exceeded that for vinyl stearate and its combinations with vinyl acetate. For these systems and for other copolymers and terpolymers<sup>15,18,31</sup> containing fatty comonomers,  $K$  was essentially zero. The reasons for this are probably mechanistic differences between the two modes of plasticization. In one view,<sup>14</sup> external plasticizers function by a twofold process. Some plasticizer molecules attach themselves to the main chain through polar attractions, thus reducing interchain forces. Other molecules, lodging in cavities created in the liquid structure, remain liquid even as the polymer chains become rigid on cooling. In this way, the  $T_g$  is additionally reduced, thus increasing the magnitude of  $K$ . In contrast, the plasticizing segments of random interpolymers appear to act simply as diluents in lowering the glass transition temperature.

Simple dilution can be considered as arising from the accumulation of free volume around the segments comprising chain ends in the glassy matrix. The effect on lowering  $T_g$  by accumulated chain-end imperfections, first proposed by Fox and Flory,<sup>32</sup> is stated as

$$T_g = T_{ga} - c/\bar{M}_n \quad (8)$$

where  $T_{ga}$  is the glass transition temperature for a polymer of infinite molecular weight having no chain ends,  $\bar{M}_n$  is the number-average molecular weight, and  $c$  is a constant. Equation (8) was rederived<sup>31</sup> to apply to simple random copolymers having units composed of long linear side chains, which can act as chain ends in disturbing the liquid structure. The equation became

$$T_g = T_{ga} - c_p(w_a/MW_a) \quad (9)$$

where, in the general case,  $T_{ga}$  was taken as the glass transition temperature for the stiff homopolymer,  $w_a$  was the weight fraction of plasticizing co-

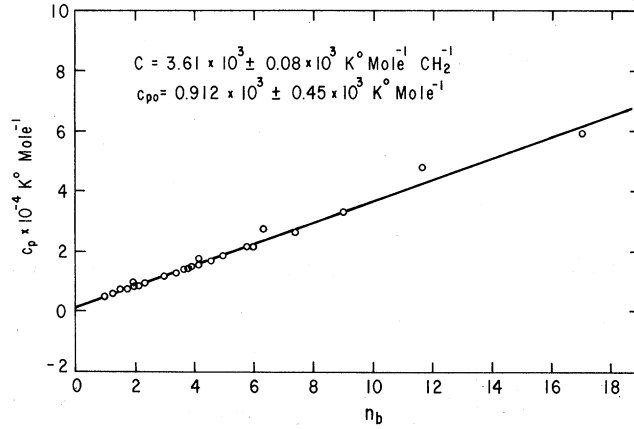


Fig. 4. Plot of  $c_p$  vs. weighted composite vinyl stearate-vinyl acetate side-chain length  $n_b$ .

monomer,  $MW_d$  was the molecular weight of its unit, and  $c_p$  was defined as  $kMW_d$ , where  $k$  was that of eq. (3). The quantity  $c_p$  for a homologous series was shown to be<sup>31</sup>

$$c_p = c_{p0} + C(n) \quad (10)$$

where  $n$  is the number of methylene groups (including terminal methyl) in the side chains. In using eq. (10) for terpolymer systems like the present, the side chain length  $n$  must recognize contributions from both esters. Consequently, in eq. (10),  $n$  becomes  $n_b$ , and in eq. (9),  $MW_d = MW_b$ . Both quantities are defined and their values listed in Table I. By insertion of these quantities from the table,  $c_p$  for the terpolymers may be calculated using

$$c_p = [(T_g - T_{ga})/w_b]MW_b \quad (11)$$

with  $T_g$  calculated by eq. (4). A plot of  $c_p$  versus  $n_b$  is shown in Figure 4, together with data for the copolymers of vinyl stearate ( $n_b = 17$ ) and vinyl acetate ( $n_b = 1$ ). These were obtained as the product  $kMW_b$ , using values of  $k$  in Table III. It may be concluded that the functional contributions of the side chains of both vinyl esters are responsible in terpolymers for the reduction in  $T_g$  as the ester content of the system increases.

The free volume  $\phi$  associated with chain ends may be obtained from  $c_p$  by employing a modified<sup>31</sup> equation of Bueche,<sup>33</sup>

$$c_p = \rho N \phi / \alpha \quad (12)$$

where  $\rho$  is the density of the homopolymer,  $N$  is Avogadro's number, and  $\alpha$  is the expansion coefficient difference between the liquid and glassy states. The free volume contributed by each side-chain methylene was shown to be

$$\phi_n = C / [\rho N (1/\alpha)] \quad (13)$$

with  $C$  from Figure 4 and  $\alpha$  from reference 31. The value of  $\phi_n$  was  $1.7 \text{ \AA}^3$ , close to that obtained for simple copolymers. Consequently, the additive effect of the free volume associated with each methylene group is alone responsible for the reduction in  $T_g$ . In externally plasticized systems the mechanism is apparently more complex.<sup>2,14</sup> The manner in which simple dilution by the plasticizing counts affects mechanical properties will be considered next.

### Relationship of Mechanical Properties to Terpolymer Composition

The experimental relation of tensile moduli and strengths to the weight fraction of vinyl stearate is shown in Figures 5 and 6. The three regions of viscoelastic behavior are clearly delineated in both figures. The relatively flat lines at the left in the figures represent the glassy region, the steep drop in modulus the transition region, and the flat portion the rubbery plateau and flow region. Systems having a vinyl acetate composition in the vinyl acetate-vinyl chloride copolymer of between zero and 0.25 mole fraction (Table I) have curves that are clustered together (curves 1-4). Only in systems where the vinyl acetate content has been increased to between 0.4 and 0.8 (curves 5, 6, and 7) is there a progressive shift of the transition region to lower compositions of vinyl stearate in both tensile moduli and strengths. The slopes in the transition region are roughly

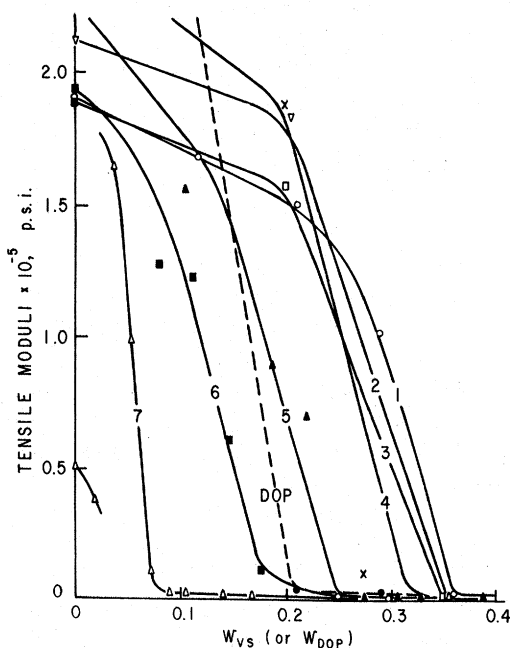


Fig. 5. Plot of tensile moduli vs. weight fraction of vinyl stearate,  $w_{vs}$ . Designations, given as mole fractions of vinyl chloride in feed, are: (1) 1-0.25 (experiments 1 through 15 of Tables I and II); (2) 0.85; (3) 0.80; (4) 0.75; (5) 0.60; (6) 0.40; (7) 0.20. Dashed line represents DOP mixtures.



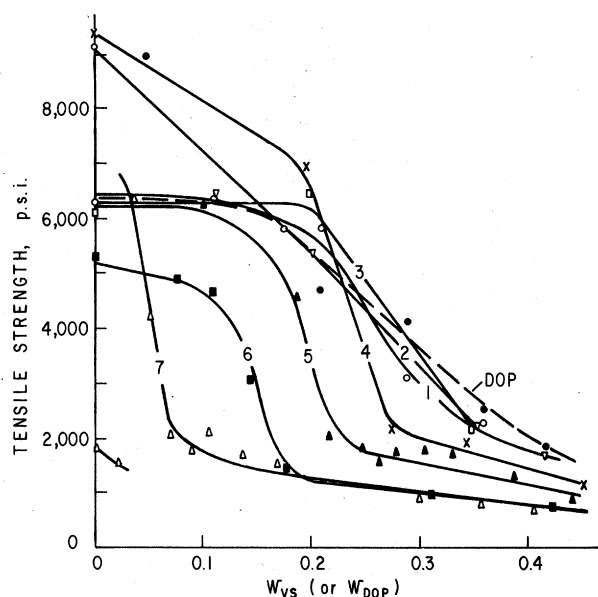


Fig. 6. Plot of tensile strengths vs. weight fraction of vinyl stearate,  $w_{vs}$ . Designations, given as mole fraction of vinyl chloride in feed, are: (1) 1-0.25 (experiment 1 through 15 of Tables I and II); (2) 0.85; (3) 0.80; (4) 0.75; (5) 0.60; (6) 0.40; (7) 0.20. Dashed line represents DOP mixtures.

parallel. A similar pattern is followed by the flexural moduli and strengths (Table II), not shown graphically. In the rubbery region, the decline in tensile moduli with composition was slow (Table II) and was similar for all systems. This is not seen clearly because the log form of the ordinate was not used in the figures. The data in this region are only approximate, however. The dashed line in both figures positions the data for the externally plasticized compositions. The anomalously large tensile value of 9000 psi found at  $w_{DOP}$  of 0.048 (experiment 53, Table II) in Figure 6 might reflect an enhancement of crystallinity produced by relaxations of the amorphous phase. Anomalous increases in moduli in the same concentration range had been noticed by others.<sup>3</sup> However, the effect could also be merely statistical.

The data in the figures were simplified, in a somewhat arbitrary fashion, to permit an orderly correlation of the transition region with respect to changes in both vinyl stearate and vinyl acetate content. This seemed to be advantageous in view of the confusion introduced by the profusion of data in Figures 5 and 6. Data for the three viscoelastic regions, glassy, transition, and rubbery, were separately correlated by computer versus weight fraction of vinyl stearate, in accordance with the relation

$$A = A_0 + Bw_{vs} + B'(w_{vs})^2 + \dots \quad (14)$$

where  $A$  is the mechanical property,  $A_0$  is the mechanical property for poly(vinyl chloride), and  $B$  and  $B'$ , etc., are the coefficients of the first and

higher degrees in  $w_{VS}$ . Only the first-degree polynomial was found to be significant. The data for the glassy region for all seven systems were correlated together to produce a single relation; a similar procedure was followed for the network data. In contrast, the transition data of each set were separately correlated. The specific designations for the mechanical properties, following the form of eq. (14), are: Intercepts:  $E'_{t0}$ , tensile moduli, and  $TS_0$ , tensile strength. Values of the slopes  $B$  are designated  $\gamma$  and  $\delta$  for tensile moduli and for strengths, respectively. Unprimed quantities are the glassy parameters; single and double-primed quantities are for the transition and rubbery data, respectively. Specific values for all of the constants are listed in Table III.

If an average of the slopes  $\gamma'$  and  $\delta'$  of the transition data is taken as representing the slope for each set, a new intercept for each set may be computed. Thus, for tensile modulus  $E'_{t0}$ , for example,

$$E'_{t0 \text{ calc}} = E'_{t0} - \gamma' [(T_g - T_{g0})/-k] + \gamma'_{\text{ave}} [(T_g - T_{g0})/-k] \quad (15)$$

where  $T_g = 296^\circ\text{K}$  and the quantity  $(T_g - T_{g0})/-k$  is the computed  $w_{VS}$  at a  $T_g$  of room temperature. The quantities  $E'_{ts}$ ,  $\gamma'$ , and  $\gamma'_{\text{ave}}$  are from Table III. Values of  $E'_{t0 \text{ calc}}$  are also given in the table; these decrease steadily as vinyl chloride is replaced by vinyl acetate in each set. With these simplifications, the computed tensile moduli and strengths for the three viscoelastic regions are given in Figures 7 and 8. The clustering of the data at high vinyl chloride content is preserved, but the rate of change in the transition region is taken to be constant. It is of interest that the slope for the glassy region of the tensile moduli curve,  $\gamma$ , has a value ( $3.68 \times 10^5$  psi) similar to that found for copolymers of both *n*-octadecyl acrylate and methyl methacrylate ( $3.51 \times 10^5$  psi)<sup>31</sup> and for terpolymers of *n*-octadecyl and ethyl acrylate with acrylonitrile ( $3.77 \times 10^5$  psi)<sup>18</sup>. From the position of the dashed line (DOP + VCL) in Figure 7, it is seen that a proper selection of the base copolymer can be made to compensate for the poorer plasticizing efficiency of the interpolymers in reducing modulus. However (Fig. 8), the tensile strength of the terpolymers was reduced to lower values over shorter ranges of composition than was that of the DOP mixtures (dashed line). This suggests that crystalline networks in the externally plasticized system<sup>3-11</sup> maintain tensile strength without affecting moduli. It is known that transient crosslinks contribute to orientation stabilization,<sup>34</sup> thereby increasing tensile strength. Insoluble diluents, on the other hand, promote instability and premature failure. In the copolymers and terpolymers of this study, the long side chains are thought<sup>31</sup> to exist as aggregates in the polymer matrix because of unfavorable free energy of mixing with the main chain units. Aggregates intensify deformation instability by acting as stress concentrators, especially at concentrations permitting side-chain crystallinity. Thus, brittle failure<sup>34</sup> and low elongations characterize much of the failure in the glassy polymers and those having large vinyl stearate contents (Table II).

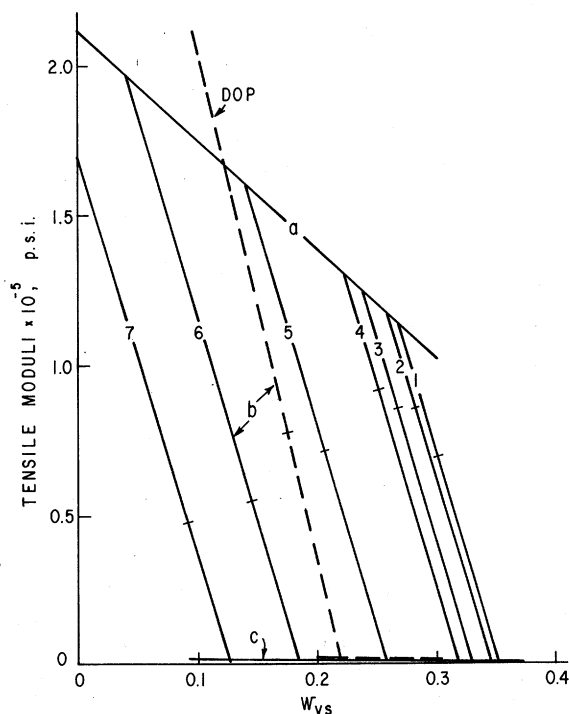


Fig. 7. Plot of calculated moduli vs. weight fraction of vinyl stearate,  $w_{vs}$ , for the glassy region (a), the transition region (b), and the rubbery plateau (c). Designations, as mole fraction of vinyl chloride in feed, are: (1) 1-0.25 (experiments 1 through 15 of Tables I and II); (2) 0.85; (3) 0.80; (4) 0.75; (5) 0.60; (6) 0.40; (7) 0.20. Dashed line represents DOP mixtures. Slashes represent compositions where  $T_g$  corresponds to room temperature.

### Thermal and Photostabilization

The presence of vinyl stearate introduced considerable photostability into these compositions. This can be seen in Figure 9. The data at the left in the figure are for unstabilized polymers containing no additives; those at the right contain 3% stabilizer. The two sets of samples had similar histories of thermal treatment. It is apparent that vinyl stearate contributes considerable retardation of photodegradation compared to vinyl acetate. Dilution by the extra volume of the long side chains cannot account for the results.

Let us consider the unstabilized examples. The 0.25 mole fraction vinyl acetate copolymer, for example (Fig. 9, line 4), was considerably more degraded than the 0.10 mole fraction vinyl stearate copolymer (line 3). Both have similar weight fractions of plasticizing comonomer (Table I), but the statistically long sequence lengths of vinyl chloride segments<sup>35</sup> are even more reduced in the former system. Similarly, PVC diluted by 36 weight-% DOP (last line) is considerably less stable than the same 10

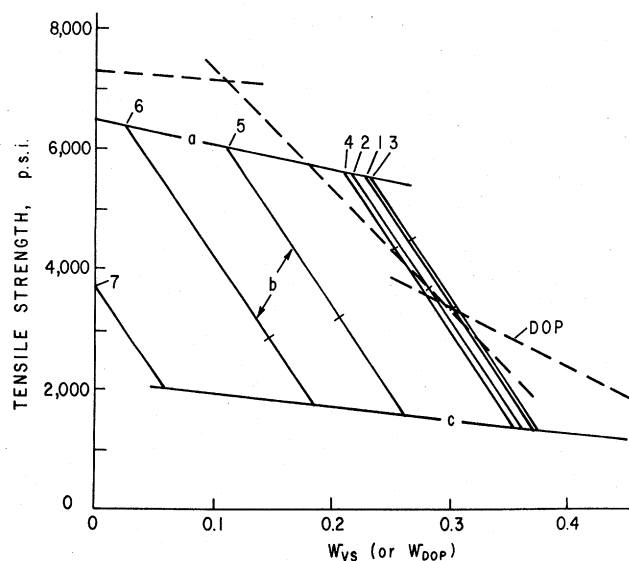


Fig. 8. Plot of calculated tensile strengths vs. weight fraction of vinyl stearate,  $w_{VS}$  for the glassy region (a), the transition region (b), and the rubbery region (c). Designations, as mole fraction of vinyl chloride in feed, are: (1) 1-0.25 (experiments 1 through 15 of Tables I and II); (2) 0.85; (3) 0.80; (4) 0.75; (5) 0.60; (6) 0.40; (7) 0.20. Dashed line represents DOP mixtures. Slash marks represent composition at which  $T_g$  corresponds to room temperature.

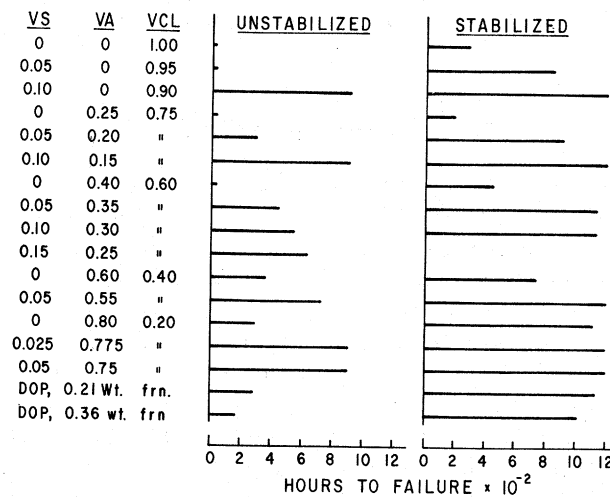
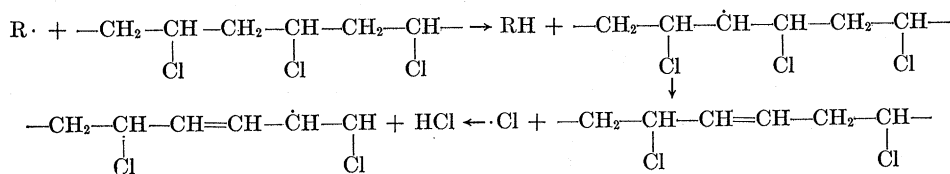


Fig. 9. Relative stabilization in the xenon arc Weather-Ometer test of poly(vinyl chloride), selected base vinyl acetate-vinyl chloride copolymers, selected terpolymers, and selected DOP mixtures. Sample at top of stabilized list was a commercial poly(vinyl chloride)-poly(vinyl acetate) copolymer, 87-13 weight-%. Systems are designated as feed mole fraction.

mole-% vinyl stearate copolymer, which contains about 35 weight-% of vinyl stearate. The effect for the terpolymers follows the same trends, except that more stabilization is introduced into the base copolymers as their sequence distributions shift to shorter segmental runs of vinyl chloride. Some experimental anomalies are unexplained, such as the lower stabilities in the middle range in the figure and the difference in the last two lines. The presence of added stabilizer overwhelms the retarding effect of vinyl stearate. Even in these data, however, vinyl stearate can be seen to effectively retard photodegradation.

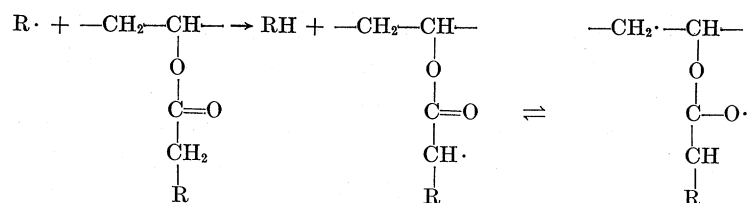
The mechanism of thermal, photo-, and radiation degradation of PVC is far from settled.<sup>36-38</sup> However, all three types seem to operate by a similar mechanism.<sup>37</sup> Whether occurring in air or an inert atmosphere, all degradation involves dehydrochlorination from adjacent units of the poly-(vinyl chloride) chain (the so-called "zippering" effect),<sup>39</sup> producing discoloration through the accumulation of polyene structures,<sup>40</sup> with chain scission and crosslinking occurring on prolonged exposure,<sup>41,42</sup> especially in air.<sup>42,43</sup> Accumulated hydrogen chloride does not catalyze the thermal degradation in inert atmospheres<sup>44</sup> but does increase the rate in oxygen<sup>41,45</sup> and under photolysis.<sup>42</sup> Thermal stabilization appears to be accomplished by the synergistic interaction of cadmium and barium salts acting to esterify thermally labile sites. Epoxide structures additionally etherify the same sites under cadmium chloride catalysis.<sup>46</sup> However, this stabilization mechanism, and others like it,<sup>47</sup> favor intermolecular eliminations as the operating mode of dehydrochlorination. Many authors,<sup>37</sup> however, favor a radical-chain mechanism. Under such a mechanism, antioxidants<sup>48</sup> and other radical scavengers<sup>37</sup> can stabilize against both thermal and photolytic degradation.

All investigators agree<sup>37</sup> that photolytic degradation proceeds via a radical mechanism. The mechanism of Winkler<sup>49</sup> has received wide acceptance. In this scheme, propagation proceeds as follows:



where the initiating species,  $\text{R}\cdot$ , involves reactive radicals of the type  $\text{CH}_2\text{—CH}\cdot$ ,  $\text{Cl}\cdot$  formed in an inert atmosphere,<sup>50</sup> and  $\text{OH}\cdot$  and  $\text{CH—CH}_2\cdot$ ,  
 $\begin{array}{c} | \\ \text{Cl} \end{array}$

formed additionally in air.<sup>51</sup> Termination employs the highly reactive primary radicals together with combinations of macroradicals. The stabilization effect of vinyl stearate can be explained as proceeding through preferential radical attack at the  $\alpha$ -carbon atom<sup>52</sup> to produce a radical of greater stability than the initiating radicals  $\text{R}\cdot$ , as follows:



While vinyl acetate would also participate in the above reaction scheme, effective chain transfer has been shown<sup>52</sup> to be higher with the longer acyl group. In further support, chain transfer to reactive radicals was found to be high for the stearate group compared to acetate.<sup>28</sup> The stabilized radicals thus formed will tend to terminate by combination. Another possibility involves oxygen attack at the  $\beta$ -position of the stearate side chain to produce a hydroperoxide.<sup>53</sup> This, on decomposition, could yield stabilized cleavage products but would also produce a hydroxyl radical. Many other possible mechanisms can probably be written. Consequently, considerable effort will have to be expended to establish the reaction path for the enhancement of the retardation of degradation by the presence of vinyl stearate units in the polymer chain.

## CONCLUSIONS

It may be concluded from the data in this paper that DOP was a more efficient plasticizer than vinyl stearate. However, after introduction of 40 mole-% or more of vinyl acetate into terpolymers, given weights of vinyl stearate could achieve glass temperatures as low as or lower than those resulting from equal weights of DOP in poly(vinyl chloride) alone. In the terpolymers, moduli were reduced to low levels at relatively low vinyl stearate contents. However, ultimate strengths and elongations for these terpolymers were considerably lower than for the simple DOP mixtures at comparable compositions. Future work in nonvolatile plasticization will require design of systems having a relaxation-time distribution similar to DOP mixtures in the rubbery region of viscoelasticity. Reinforcement through crystallinity retained in the externally plasticized systems is responsible for this distribution and hence for the superior mechanical properties of externally plasticized polymers.

Vinyl stearate exerted considerable retardation of photolytic degradation compared to both vinyl acetate and the external plasticizer. The effect was greater than could be ascribed to simple dilution by the long alkyl groups. A mechanism producing a stearyl radical more stable than the initiating species was suggested.

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Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

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